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Cu-ZSM-5/Ni net composite used as DeNO$_x$ catalyst

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ZSM-5 was directly grown on a preshaped Ni net support and subsequently exchanged with Cu^{2+} ions, then the supported Cu-ZSM-5 was employed as a NO reduction catalyst. The supported catalyst was found to show an activity comparable to that of an unsupported Cu-ZSM-5 zeolite. Furthermore, the hydrothermal stability of the CuZSM-5 was greatly improved when grown on the Ni net support.

Keywords: CuZSM-5, Ni net, composite, DeNO$_x$, catalyst

1. Introduction

The field of catalytic technology for environmental protection has grown rapidly in the past decade, and many of the advances have been stimulated by developments in material science. Commercial automotive exhaust catalysts are based on Rh, Pd, Pt/Al$_2$O$_3$ supported on honeycomb monoliths, which simultaneously treated carbon monoxide, uncombusted hydrocarbons and oxides of nitrogen [1]. Due to the pioneer work of Iwamoto [2] and Held [3], Cu-ZSM-5 zeolite has been found to possess higher activity and to be more stable than the traditional catalysts reported so far. However, it is also known that Cu-ZSM-5 catalysts deactived rapidly under lean-burn conditions [4,5], and it has been proved that migration of aluminum and copper in the zeolite channels plays a crucial role in the deactivation of Cu-ZSM-5 [6,7]. Steam treatment can induce dealumination, and thermal treatment at high temperatures can cause agglomeration of copper on the zeolite surface and channels, both resulting in the deactivation of the catalyst. In order to stabilize the activity for NO removal in the presence of water, ZSM-5 was grown *in situ* on Raney Ni. The Al source for synthesizing the zeolite is the residual Al in the Raney Ni, and the hydrothermal and thermal stabilities were greatly improved in the SCR of NO$_x$ with ammonia [8].

Environmental catalysts have to work under very severe conditions, such as wide temperature range, high space velocity, low concentration of target materials, high concentration of co-existing gases and poisons. In other words, environmental catalysts must have extremely high activities, selectivities, and durabilities. The catalyst shaping is also an important issue for environmental catalysts, which needs to balance performance, strength and pressure drop across the catalyst system. Calis et al. reported that ZSM-5 crystals could be grown *in situ* on the surface of a stainless-steel gauze, which was preshaped as rolls in the zeolite synthesis mixture. The wire thickness was 35 μm and the zeolite loading was about 3.5%. Copper ions were exchanged into the zeolite, which was found to show improved SCR activity and selectivity compared with a conventional catalyst consisting of Ti and V, and supported on amorphous silica [9]. In the present paper, we developed a novel structure of zeolite packing, with high DeNO$_x$ activity and stability. The novel catalyst packing consisted of the preparation of thin layer Raney Ni on a Ni net, and the growing of ZSM-5 *in situ* on it. The packing was made catalytically active by the introduction of copper through ion exchange. The DeNO$_x$ activity and stability of the catalyst with ammonia as the reductant in the presence of excess oxygen were investigated; the results showed a promising future for commercialization of the catalyst.

2. Experimental

2.1. Preparation of the catalysts

Preparation of the Cu-ZSM-5/Ni net composite involved pretreatment of the support material, zeolite synthesis, calcination, and ion exchange. Ni net (Goodfellows, 63 mm × 32.5 mm, wire diameter 18 μm, 70 wires per inch) were pretreated with 0.1 N HCl, followed by washing with deionized water. 10 000 Å thickness of Al was sputtered on both sides of the Ni mesh, subsequently it was heated in argon at 1153 K for 1 h to form a thin layer of Ni–Al alloy. At last, it was leached with 50 ml NaOH (6 M) at 363 K for 1.5 h followed by leaching in an autoclave with 15 ml NaOH (1 M) at 453 K for 48 h. Zeolite was grown on the Ni mesh from a synthesis solution containing sodium silicate (Merck, 27 m% SiO$_2$, 14 m% Na$_2$O), TPABr (Merck), and distilled water. The molar composition was

$$Na_2O : 100SiO_2 : 10TPABr : 7000H_2O.$$

The Al source of the zeolite synthesis was the Al$_2$O$_3$ existing on the surface of the leached Ni gauze wire.

15 ml synthetic mixture and the Ni mesh were introduced into a 25 ml autoclave. The synthesis was performed at 453 K for 48 h, at autogenic pressure. The samples were washed with distilled water, dried at 393 K for 12 h and calcined at 773 K for 10 h. Subsequently, the Na-form zeolite composite was transformed to the H-form zeolite composite by the usual ion-exchange method, using an NH_4OH aqueous solution (1 M, Merck), followed by washing with distilled water. Copper ions were introduced by exchange with an aqueous 0.01 M copper acetate solution at room temperature, three times consecutively for 24 h, each time with fresh solution. Finally, the sample was dried in air at 393 K for 24 h. The Cu-ZSM-5/Ni net composite was shaped in rolls, and put into the U-tube reactor. The tested Cu-ZSM-5/Ni mesh composite had a total mass of 0.557 g, consisting of 93.3% mass support material, 6.7% mass ZSM-5 type zeolite.

2.2. Characterization and evaluation of the catalysts

Powder X-ray diffraction data were collected on a Siemens D5000 diffractometer using the Cu Kα line. The SEM microscope used was a HITTACH 4000 scanning electron microscope. A stainless-steel microreactor set-up equipped with six gas lines was built for the catalytic testing. The flows of Ar, NO/Ar, NH_3/Ar, and O_2/Ar were controlled by mass flow controllers. N_2, NH_3, H_2O, and O_2 were analyzed by a calibrated mass spectrometer, and a combined non-disperse IR/UV detector was used for the determination of NO and NO_2. The reduction of nitric oxide with ammonia was carried out under atmospheric pressure in a U-tube reactor of 6 mm i.d. A piece of zeolite-loaded gauze (0.557 g, including 37 mg zeolite on the gauze) was rolled and put into a quartz reactor tube. Before the reaction, the catalyst was heated in Ar at 673 K for 2 h to remove adsorbed water. On the other hand, 37 mg unsupported Cu-ZSM-5 was also evaluated under the same conditions for comparison. The preparation of Cu-ZSM-5 was described elsewhere [10]. The standard concentrations of reactants were 500 ppm for both NO and NH_3 and 0.9% for O_2, the balance was Ar. The total flow rate was 120 ml/min. For the data reported:

$$\text{NO conversion\%} = \left[(\text{NO}_{\text{in}} - \text{NO}_{\text{out}})/\text{NO}_{\text{in}}\right] \times 100\%,$$

$$\text{NO}_2 \text{ yield\%} = (\text{NO}_2/\text{NO}_{\text{in}}) \times 100\%,$$

$$\text{NH}_3 \text{ conversion\%} = \left[(\text{NH}_{3\text{in}} - \text{NH}_{3\text{out}})/\text{NH}_{3\text{in}}\right] \times 100\%,$$

$$\text{N}_2 \text{ yield\%} = \left[2\text{N}_2/(\text{NH}_{3\text{in}} + \text{NO}_{\text{in}})\right] \times 100\%.$$

3. Results and discussion

After the zeolite crystals were grown *in situ* on the Ni net, the Ni surface was examined by SEM, as shown in figures 1 and 2. It is obvious that almost all the area of the Ni surface was covered with zeolite crystals, and the average size of the crystals was about 2–3 μm in diameter. In order to examine the type of the zeolite, the crystals grown on the Ni net were scraped for XRD detection. As can be seen in figure 3, the peak positions and the intensity ratios of the peaks were in good agreement with an XRD pattern of ZSM-5 [11], confirming the growth of ZSM-5 on the Ni gauze support. The crystals observed in figures 1 and 2 are in typically elongated prismatic shape. The diameter of the Ni gauze wire increased from 18 to 100 μm after the growing of zeolite on it. This result suggested that about 40 layers of mean thickness of ZSM-5 were grown on the Ni net. For the application of the zeolite packing, it is better to grow as much as possible zeolite per weight of support. The zeolite crystals are difficult to be scraped from the surface of the Ni net, and the reason may be that the Al component all comes from the Raney Ni on the Ni net, and the thus formed zeolite crystals are chemically bonded with the surface of the Ni gauze wire [8]. According to the EDX result, there are about 2% mass Al as compared with the Ni on the surface of the Ni mesh.

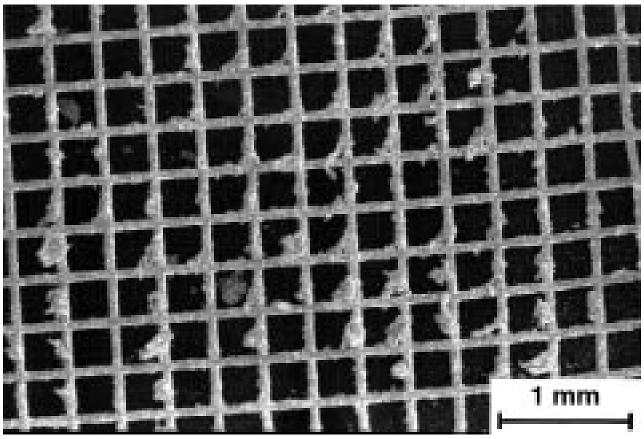

Figure 1. SEM photo of zeolite grown on Ni net support (5 × 10).

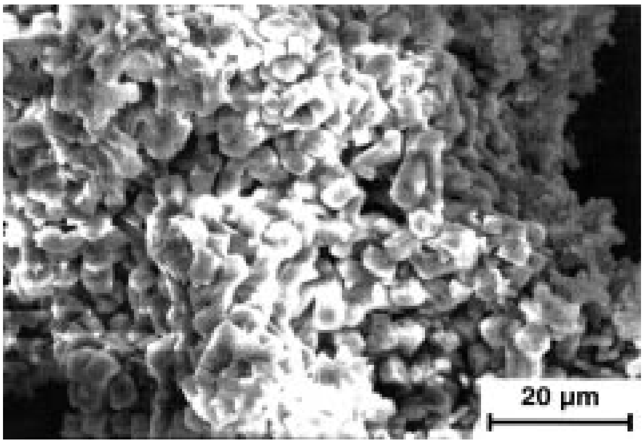

Figure 2. SEM photo of zeolite crystals grown on Ni net support (5×500).

The catalytic activities of the Cu-ZSM-5/Ni net catalysts in NO reduction with ammonia under oxygen-rich conditions were evaluated. As shown in figures 4–6, the concentrations of various reactants and products versus temperatures were recorded when the reaction reached a steady

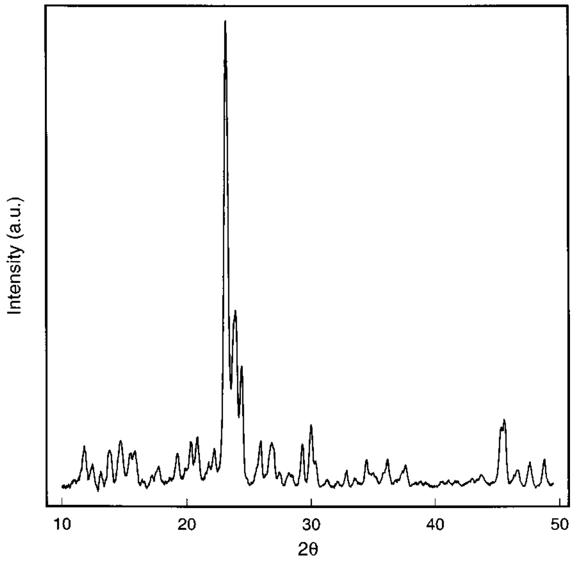

Figure 3. XRD pattern of zeolite crystals scraped from the surface of Ni net.

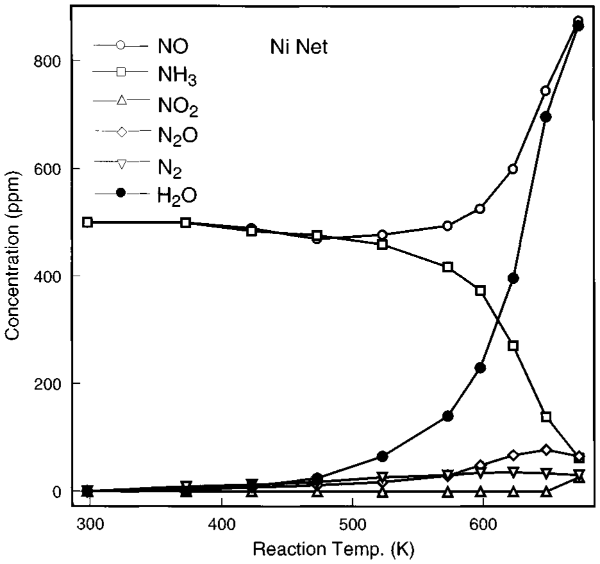

Figure 4. Product distribution of NO reduction versus temperatures on Ni net catalyst.

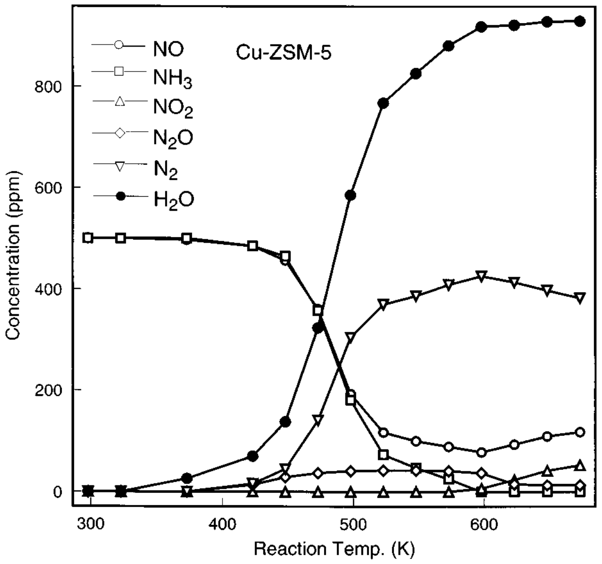

Figure 5. Product distribution of NO reduction versus temperatures on Cu-ZSM-5 catalyst.

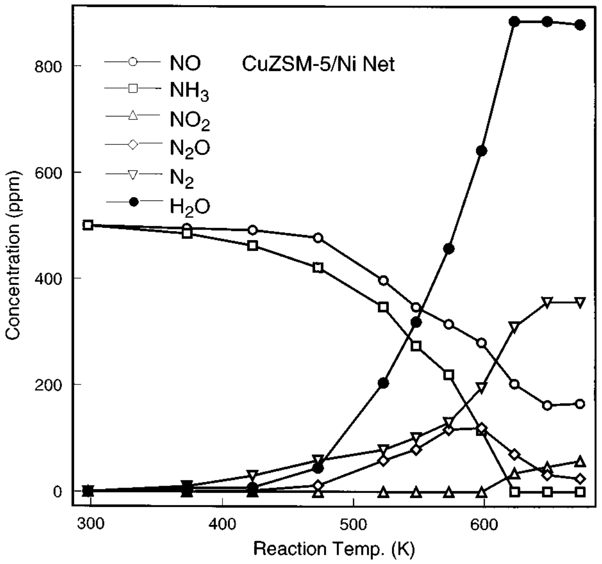

Figure 6. Product distribution of NO reduction versus temperatures on Cu-ZSM-5/Ni net catalyst.

state. The possible reactions taking place on these catalysts were as follows [9]:

$$NO + NH_3 + \tfrac{1}{4}O_2 \rightarrow N_2 + \tfrac{3}{2}H_2O \qquad (1)$$

$$NH_3 + \tfrac{5}{4}O_2 \rightarrow NO + \tfrac{3}{2}H_2O \qquad (2)$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad (3)$$

$$NH_3 + O_2 \rightarrow N_2O + H_2O \qquad (4)$$

From figure 4 it can be seen that on the Ni net reaction (2) dominates at temperatures above 500 K, so that the concentration of NO rises at the expense of NH_3 in this temperature range. There is only a small amount of N_2O, and negligible concentrations of N_2 and NO_2 produced even above 600 K, indicating that as a support the Ni net has no activity for NO reduction, and NO is difficult to be oxidized to NO_2 even at the excess of O_2.

On the other hand, the CuZSM-5 catalyst exhibited the highest DeNO$_x$ activity among the three catalysts, as shown in figure 5. The conversions of NO and NH_3 and the yield of N_2 reached their optimum values at ca. 600 K. At the same time, there was little amount of N_2O and NO_2 produced, which means that the selectivity of the catalyst is also high. The results are consistent with the previous reports [12–14] in which Cu-ZSM-5 catalyst was employed for NO_x reduction by NH_3. As for the CuZSM-5/Ni net, the activity and selectivity were a little lower than those of the unsupported CuZSM-5, as can be seen from figure 6. This may be due to the negative influence of the Ni net support on which NH_3 is readily oxidized to NO above 500 K,

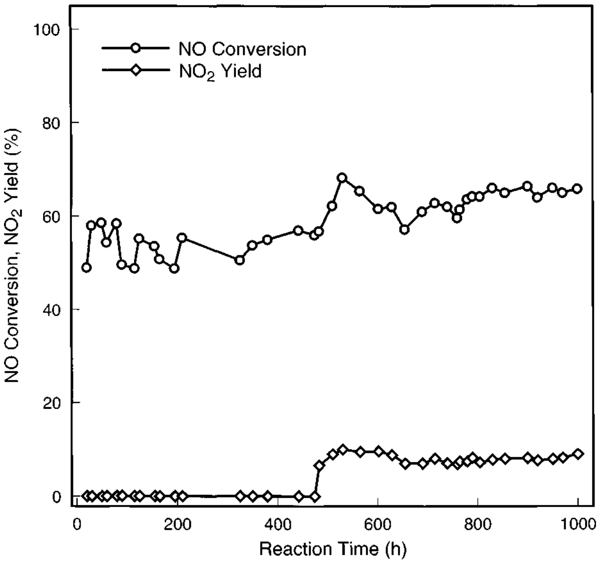

Figure 7. The activity of Cu-ZSM-5/Ni net catalyst at 600 K within 1000 h reaction.

resulting in a net consumption of NO. The stability of the catalyst is unexpectedly high, as evidenced by figure 7, and the activity for DeNO$_x$ was not decreased even after 1000 h reaction. However, the selectivity was lowered to some degree after ~500 h reaction, when NO_2 was formed in the products, which might result from the reaction between NO and O_2. It is well known that unsupported CuZSM-5 was readily deactivated when there was water in the reaction system [15]. In the present case, the concentration of water exceeds 800 ppm when the reaction reaches a steady state at above 600 K. The improvement of hydrothermal stability of the CuZSM-5 after being supported on the Ni net may also be ascribed to the strong chemical bond formed between the zeolite crystals and the Raney Ni existing on the surface of the Ni net [8].

4. Conclusions

ZSM-5 was successfully grown on a Ni net support. The supported zeolite with exchanged Cu^{2+} cations was employed in a model reaction of NO reduction with NH_3 in the presence of excess oxygen. It exhibited activity comparable to that of unsupported Cu-ZSM-5. Most important is that the hydrothermal stability was much higher than that of the unsupported Cu-ZSM-5. The present approach to grow zeolite directly on a support offers a new possibility to apply zeolite efficiently on a metal monolith which is applicable to NO$_x$ emission control of mobile sources.

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